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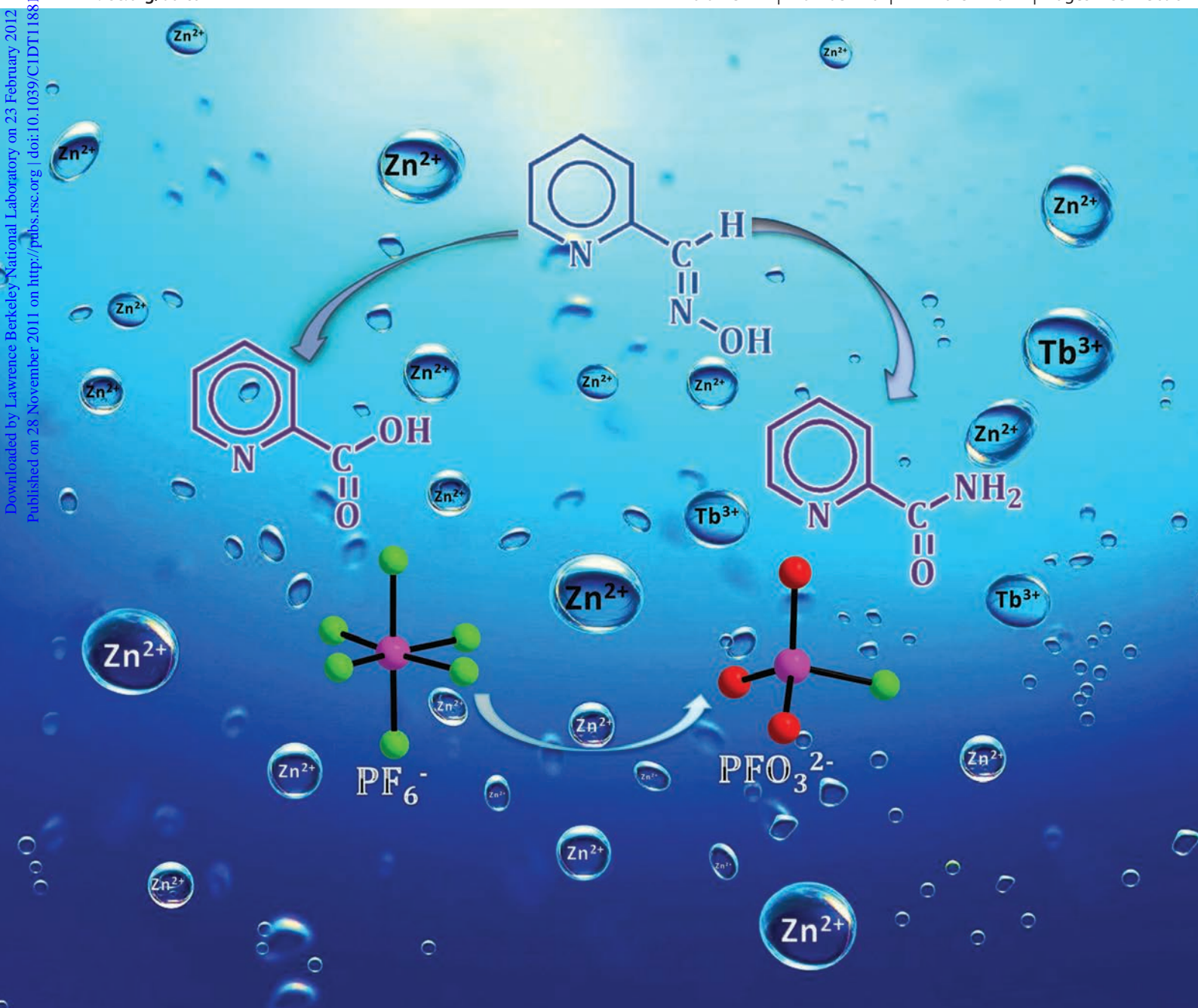
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Metal ion-assisted transformations of 2-pyridinealdoxime and hexafluorophosphate†

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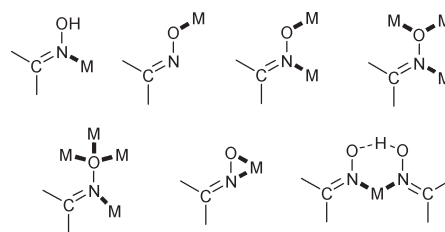
Metal-ion mediated reactions of 2-pyridinealdoxime and hexafluorophosphate lead to Zn^{II} complexes containing picolinic acid, picolinamide and monofluorophosphate (−2) as ligands.
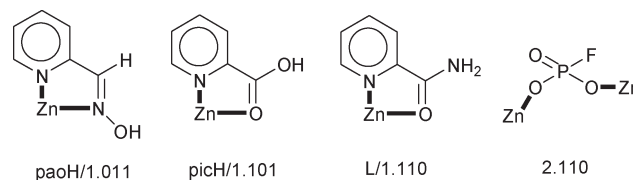
Whilst the effect of the field exerted by ligands on a metal ion is well understood and can be satisfactorily quantified, the obverse situation of the role of the metal ion is not, for a number of reasons.[1] Upon coordination of a ligand (L) to a metal (M) centre, the ligand's properties (such as electrophilic or nucleophilic character, acidity, susceptibility to oxidation or reduction, *etc.*) can be significantly altered, thereby enhancing or inhibiting its reactivity. Coordination to a metal centre can even enable a reaction that would otherwise not take place.[2] Thus the altered reactivity of ligands as a result of their ligation to a metal ion M is currently a "hot" research theme in modern transition-metal chemistry,[1–4] where the use of metal complexes as stoichiometric reagents and also as homogeneous catalysts in organic chemistry is being explored. Among the factors affecting ligand (L) reactivity are the electron-acceptor/donor properties of the individual M and L partners, as well as the nature of any co-ligands. Reactions occurring upon coordination can involve nucleophilic or electrophilic addition to ligands, acid–base reactions, internal redox reactions between L and M, L coupling, template synthesis, rearrangement of ligands, stabilisation of unstable species and protection of functional groups by metal centres.[2] For example, oxime and oximate groups can bind a metal ion in a variety of coordination modes (Chart 1).[5,6a] A coordinated oxime contains three potentially reactive sites (C, N and O atoms) and an –OH group, the acidity of which increases upon coordination. Nucleophilic reagents can add to the *C*-atom (a reaction that is promoted by coordination of the *N*-atom), whereas electrophilic reagents can attack the *O*- or the *N*-sites.[5,7]

Chart 1 The crystallographically confirmed coordination modes of the oxime and oximate groups.

Our groups have a long-standing interest in the reactivity of coordinated ligands,[3,6,8] and especially in metal-mediated reactions of 2-pyridyl oximes (Fig. S1†).[6a,9] Furthermore, the anions of 2-pyridyl oximes are versatile ligands for a variety of research objectives[6a,10] and 2-pyridinealdoxime (IUPAC name: 2-pyridine-2-carbaldehyde oxime, paoH; Chart 2) occupies a special position amongst the 2-pyridyl oximes because (i) it is the simplest and most flexible 2-pyridyl oxime,[11] (ii) it is the only *aldoxime* in this family, and (iii) its anionic form, pao$^-$, is a key ligand in the area of single-chain magnetism.[12] However, its metal-mediated reactivity remains (with one exception[9b]) unexplored. In the present work, we report three reactions of paoH with Zn^{II} sources; in two products novel/rare transformations of paoH have been observed, while in the third an interesting hydrolysis reaction of PF$_6^-$ has taken place. We believe this

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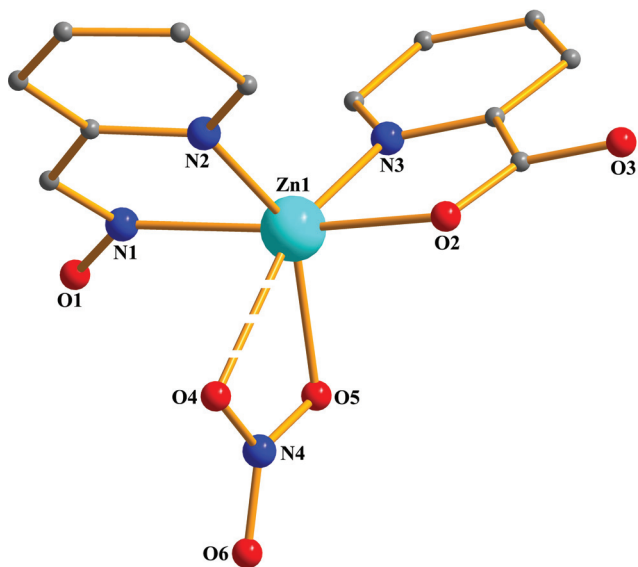*[e] Advanced Light Source, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA94720, USA*
[f] Institute of Chemical Engineering and High Temperature Chemical Processes, Foundation for Research and Technology-Hellas (FORTH/ ICE-HT), Platani, P.O. Box 1414, GR-265 04 Patras, Greece
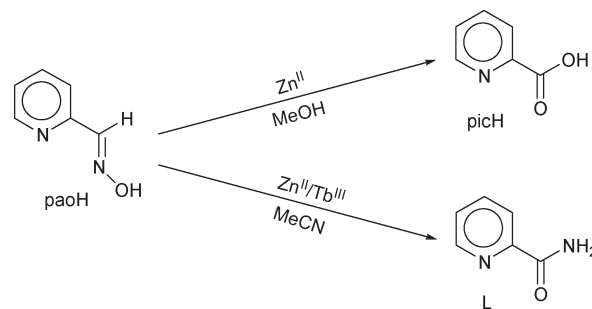† Electronic supplementary information (ESI) available: Full experimental synthetic (text), crystallographic (text, Table S1) and structural (Tables S2–S4, Fig. S1, S2 and S4) details, and simplified mechanistic views (Figs. S3 and S5). CCDC reference numbers 846480 (**1**), 846481 (**2**) and 846482 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11881a

Chart 2 Abbreviations and coordination modes of the organic ligands discussed in the text; the ligation mode of PO$_3$F^{2-} in complex **3** is also shown.

work presages a rich new area of metal-assisted reactivity of paoH.

The reaction of $Zn(NO_3)_2 \cdot 4H_2O$ and paoH in an 1:2 molar ratio in MeOH under reflux gave a pale yellow solution that upon storage at room temperature gave colourless crystals of $[Zn(NO_3)(paoH)(picH)](NO_3)$ (**1**), where picH is picolinic acid, in 55% yield. The IR spectrum of the product shows an intense band at 1680 cm^{-1} attributed (with hindsight) to $\nu(C{=}O)$. The same reaction in absolute MeOH under anaerobic conditions affords a solid, whose analytical data correspond to the formula $Zn(NO_3)_2(paoH)_2$ and IR spectrum confirms the absence of picH. Complex **1** crystallises‡ in the triclinic space group $P\bar{1}$. The Zn^{II} centre in the very distorted octahedral cation $[Zn(NO_3)(paoH)(picH)]^+$ (Fig. 1) is coordinated by one anisobidentate nitrato group [Zn–O5 = 2.071(3) Å, Zn–O4 = 2.473(3) Å], one 1.101 (Harris notation[13]) N,N'-chelating paoH ligand (Chart 2) and one 1.101 N, O-chelating picH molecule. In the crystal lattice there are hydrogen bonds with the oxime and protonated carboxylic oxygens as donors and two ionic nitrate oxygens as acceptors resulting in the formation of "tetrameric" entities; these units are further stabilized by a π–π stacking interaction between the aromatic rings of the picH ligands (Fig. S2†). The most remarkable feature of this reaction is the *in situ* formation of the picolinic acid ligand (Chart 3). Without any mechanistic implication, we suggest that formation of **1** is triggered by hydrolysis of an amount of paoH to the corresponding aldehyde, 2-pyridinealdehyde, followed by the atmospheric oxygen oxidation of the latter to picolinic acid, picH.[14] A simplified transformation scheme is shown in Fig. S3.† The difference between regular (paoH is very stable in MeOH solutions under aerobic conditions at room temperature or at refluxing conditions as evidenced by ^1H NMR) and metal-mediated conditions lead us to believe that the hydrolysis step is Zn^{II}-assisted and most probably involves reaction of electrophilically activated coordinated oxime group with water.[14,15] The paoH → picH (albeit in its anionic form, pic^-) transformation has been observed only in Mn^{II} carboxylate chemistry.[9b]

Chart 3   The metal-mediated transformations of paoH observed in **1** and **2**.

The reaction of $Zn(ClO_4)_2 \cdot 6H_2O$, $Tb(NO_3)_2 \cdot 6H_2O$ and paoH in an 1:1:4 molar ratio in MeCN gave a pale yellow solution that upon storage at room temperature gave colourless crystals of $[ZnL_2(H_2O)_2](NO_3)_2$, where L is picolinamide, in ~50% yield. The IR spectrum of the solid shows characteristic bands at 3299, 3140 and 1660 cm^{-1} attributed (with hindsight) to $\nu_{as}(NH_2)$, $\nu_s(NH_2)$ and $\nu(C{=}O)$ modes of the coordinated primary amide group of L. Complex **2** crystallises‡ in the monoclinic space group $P2_1/c$. In the centrosymmetric distorted octahedral cation $[ZnL_2(H_2O)_2]^{2+}$ (Fig. 2), the Zn^{II} centre is coordinated by two 1.110 N,O-chelating L ligands (Chart 2) and two aqua groups. The Zn1–O1, Zn1–O2 and Zn1–N2 bond lengths are 2.073(1), 2.123(2) and 2.098(1) Å, respectively. In the crystal lattice there are a significant number of hydrogen bonds with the participation of the two H atoms of both the H_2O ligands and $–NH_2$ groups and all the NO_3^- atoms; the consequence is the formation of 2D networks (Fig. S4†). The individual reactions between $Zn(NO_3)_2 \cdot 6H_2O$ or $Tb(NO_3)_2 \cdot 6H_2O$ and paoH in MeCN give complexes $[Zn(NO_3)_2(paoH)_2]$ and $[Tb_2(NO_3)_6(paoH)_2]$, respectively.[16] Thus, the presence of both Zn^{II} and Tb^{III} seems essential to the paoH → L transformation (Chart 3) which is observed for the first time. Compound **2** joins a handful of structurally characterized Zn^{II}/L complexes[17] prepared by direct reactions of Zn^{II} sources and L.
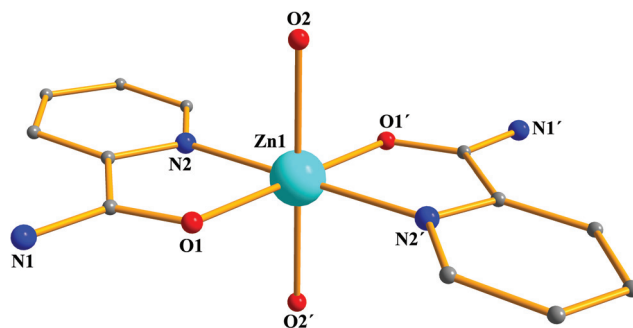

Fig. 1   The molecular structure of the cation $[Zn(NO_3)(paoH)(picH)]^+$ in the crystal of **1**. The dashed line represents a weak bond.

Fig. 2   The molecular structure of the cation $[ZnL_2(H_2O)_2]^{2+}$ in the crystal of **2**. Unprimed and primed atoms are related by the symmetry operation $1 - x, - y, - z$.

The above described reaction is a metal-mediated Beckmann rearrangement.[5,7,15b] The isomerisation of aldoximes to primary amides, *i.e.* the Beckmann rearrangement,[18] is one of the most straightforward synthetic routes to obtain amides. Typically, this isomerisation can be effected using strong acids or other activating agents, usually in stoichiometric amounts and at high

temperatures. In addition to harsh reaction conditions, one of the main drawbacks of the Beckmann rearrangement is its poor efficiency towards aldoximes often leading to the formation of nitriles.[19] Recently, the use of late transition metal ions as catalysts (both homogeneous and heterogeneous) or cocatalysts has allowed for some impovements and systems based on Ru,[20] Rh,[21] Ir,[22] Ni,[7] Zn/Co,[23] Pd[7] and Ag/Au[19] have shown interesting activities. The current mechanistic hypothesis[7,19] for the metal-catalyzed rearrangement of aldoximes involves a dehydration/hydration sequence *via* the formation of a discrete nitrile intermediate (Fig. S5†). Complex **2** can be considered as a model intermediate in a putative catalysed paoH → L rearrangement.

The reaction between $ZnCl_2$ and 2 equivs of paoH in H_2O, followed by treatment with two equivs of $NaPF_6$, gave a solution that upon storage at room temperature gave colourless crystals of $[Zn_2(PO_3F)_2(paoH)_4]$ (**3**) in 40% yield. The IR spectrum of the solid shows bands at 1191, 1112 and 846 cm^{-1} attributed (with hindsight) to $\nu(PO_3)$ [1192, 1112 cm^{-1}] and $\nu(PF)$ [846 cm^{-1}] vibrations of the coordinated PO_3F^{2-} group. Complex **3** crystallises‡ in the monoclinic space group $P2_1/n$. Its structure consists of dinuclear $[Zn_2(PO_3F)_2(paoH)_4]$ molecules located at an inversion centre (Fig. 3). The two Zn^{II} atoms are bridged by two tetrahedral *syn, anti* 2.110 PO_3F^{2-} groups (Chart 2); two 1.011 paoH ligands complete a distorted octahedral coordination at each metal site. The molecule is the *cis-cis-trans* isomer with respect to the disposition of the fluorophosphate oxygen, pyridyl nitrogen and oxime nitrogen atoms, respectively. The Zn⋯Zn distance is 5.080(3) Å. There are four intramolecular hydrogen bonds with the uncoordinated oxime oxygens (O1, O2, O1′, O2′) as donors and the "free" fluorophosphate oxygens O5 and O5′ as acceptors; thus O5 (and its symmetry equivalent) participates in two hydrogen bonds. The PO_3F^{2-} group arises from the partial hydrolysis of the PF_6^- ion ($PF_6 + 4H_2O \rightarrow PO_3F^{2-} + 5HF + H_3O^+$).[24] ^{19}F and ^{31}P NMR spectra of freshly prepared solutions of $NaPF_6$ and $NaPF_6$/paoH (2 : 1) in D_2O showed that the amount of PO_3F^{2-} present was negligible[25] and that partial hydrolysis occurs during the reaction. We believe that the presence of the zinc cation is necessary for the hydrolysis to occur. We propose that the role of the Zn^{II} centre is to promote a cationic activation of the H_2O molecule, while the H_3O^+ from the hydrolysis reaction of $[Zn(H_2O)_6]^{2+}$ can catalyze the hydrolysis of PF_6^-.[14,24] The hydrolysis stops at the PO_3F^{2-} step, probably due to the coordination of this anion to the Zn^{II} center. Only two

examples of the partial hydrolysis to PO_3F^{2-} are known in cases where a PF_6^- ion is acting as a counteranion in Cu^I and Ru^{III} starting materials.[26] Complex **3** is the third structurally characterized Zn^{II}/PO_3F^{2-} complex.[27]

In summary, the use of paoH in reactions with Zn^{II} and Zn^{II}/Tb^{III} sources has led to extremely rare (complex **1**) and novel (complex **2**), respectively, transformations of this oxime ligand, showing that metal-mediated reactions of 2-pyridyl oximes are still in their infancy; indeed, ongoing studies in our groups reveal that we have scratched only the surface of this area. Complex **3** provides a very rare example of the detection of an intermediate in the PF_6^- hydrolysis.

Acknowledgements

Notes and references

‡ Crystal data for **1**: $C_{12}H_{11}N_5O_9Zn$, M_w = 434.63, triclinic, space group $P\bar{1}$ with a = 7.6874(12), b = 9.9484(16), c = 11.4223(17) Å, α = 96.499(3), β = 96.478(4), γ = 111.272(4)°, V = 797.6(2) Å^3, T = 150(2)K, Z = 2, D_c = 1.810 g cm^{-3}, 5343 reflections collected, 3182 unique (R_{int} = 0.0304), $R1[I>2\sigma(I)]$ = 0.049, wR_2 = 0.1096 (F^2, all data). Crystal data for **2**: $C_{12}H_{16}N_6O_{10}Zn$, M_w = 469.68, monoclinic, space group $P2_1/c$ with a = 6.8777(6), b = 11.2057(11), c = 12.8526(12) Å, β = 113.523(7)°, V = 908.23(15) Å^3, T = 180(2)K, Z = 2, D_c = 1.717 g cm^{-3}, 5330 reflections collected, 1900 unique (R_{int} = 0.0210), $R1[I>2\sigma(I)]$ = 0.0241, wR_2 = 0.0685 (F^2, all data). Crystal data for **3**: $C_{24}H_{24}N_8O_{10}P_2F_2Zn_2$, M_w = 815.23, monoclinic, space group $P2_1/n$ with a = 9.1885(3), b = 12.1035(5), c = 13.9159(5) Å, β = 90.663(3)°, V = 1547.53(10) Å^3, T = 100(2)K, Z = 2, D_c = 1.749 g cm^{-3}, 12593 reflections collected, 3695 unique (R_{int} = 0.0180), $R1[I>2\sigma(I)]$ = 0.218, wR_2 = 0.0582 (F^2, all data).

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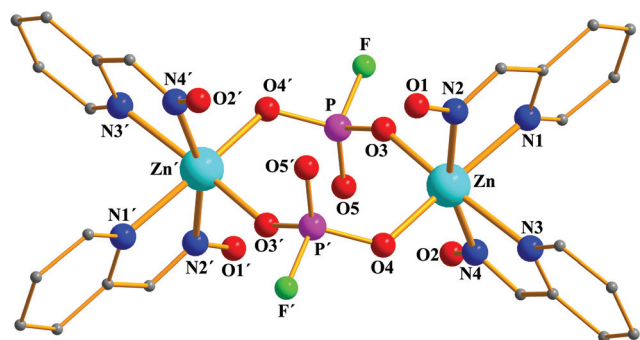
Fig. 3 The molecular structure of **3**. Unprimed and primed atoms are related by the symmetry operation −x, −y, −z.

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